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COVER: Detail of the early Middle Horizon tapestry fragment in William J Conklin's article "Peruvian Textile Fragment from the Beginning of the Middle Horizon". Photograph by Allen C. Marceron.

DRAWINGS by: William J Conklin for "Peruvian Textile Fragment from the Beginning of the Middle Horizon"; Sally Huddles for "Symbolic Scenes in Javanese Batik"; Milton Sonday for "A Type of Mughal Sash".

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PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. XIII

ACIDS AND ACID SALTS FOR TEXTILE CONSERVATION

JAMES W. RICE

ACIDS

Acids are chemicals which when dissolved in water produce hydrogen ions. These may be recognized by their sour taste but this is not a safe test because some of the acids are poisonous. Fortunately, they may be distinguished safely because they will turn blue litmus paper red and affect other pH indicators with characteristic color changes.

There are two classes from the point of view of main effect, the weak acids and the strong acids. The weak acids are relatively high on pH scale, that is, from about pH 3 to pH 6, and in this range do not damage cellulosic fibers. The strong acids are low on pH scale ranging from about pH 3 down to pH 0. Acidities in this range may be expected to destroy or damage cellulose fibers.

A second useful way of classifying the common acids is according to volatility. A volatile acid is one that escapes into the air before the destructive action on fibers or other low pH sensitive substances can take place. A nonvolatile acid would be one that concentrates on the fiber in time and eventually produces a damaging result. For this reason, volatile acids are preferred for textile usage.

The principal uses of acids in textile work are for controlling alkalinity and neutralizing residual alkalies used in cleaning textiles. Acids are also noted for their ability to set many dyes and prevent color bleeding during cleaning. Another important use for some special acids is in removal of various metal stains by dissolving them. Again, a few acids have the power of sequestering or chelating certain metallic ions within an ion complex. This is explained in part in a previous section in this Series, No. VI, The Wonders of Water in Wetcleaning, Vol. II, No. 1, December 1966.

THE WONDERS OF WATER IN WETCLEANING

The principal acids used in textile conservation are listed and described as follows in alphabetical order:

ACETIC ACID

Acetic acid (Ethanoic Acid)—CH_3COOH ($C_2H_4O_2$) probably the most widely used acid for textile conservation, is obtainable in four concentrations. At 100%, or very nearly, it is known as Glacial Acetic because it freezes at about 16.6°C (41.3°F.). At this concentration, it will dissolve cellulose acetate fibers, various resins, gums, some vegetable oils, many other organic compounds and a few inorganic elements such as phosphorus and sulfur. It is also destructive to skin tissue and should be handled with care.

Fifty-six percent (56%) concentration is a commonly available commercial variety of acetic acid. This is cheap and mainly used in making lead acetate (sugar of lead) as a step in the manufacture of white lead for paints. It is too concentrated for most textile uses and will dissolve cellulose acetate fibers and some other organic substances. Properly diluted with water, however, it becomes much safer in use.

Twenty-eight percent (28%) acetic acid, which is half of 56% acetic acid and half water, is the usual concentration for the concentrated acid prescribed by recipes and directions for spotting and other textile uses. At this point cellulose acetate is no longer affected and damaging reactions become negligible. This solution evaporates at nearly the same rate as water and for that reason excessive acidic action on textile fibers and other substances is unlikely. It does provide, however, an optimum neutralizing action for strong alkalies when needed.

For other uses, such as "souring" and dye setting, where very mild acidity is desired, the 28% variety may be diluted down to 1, 2, 3, or 4% according to the particular job to be done.

When the more concentrated solutions of acetic acid are not readily available, one may substitute white vinegar, a solution of 5% acetic acid, for such uses as souring and dyesetting. White vinegar is not concentrated enough to be satisfactory for spotting and special stain removal uses, however. Wine and other colored vinegars are not recommended because of residual staining possibilities.

"Souring", a term used to describe removal of residual alkalinity and adsorbed oxidizing bleaches after laundering, is usually accomplished by adding enough acetic acid to the final rinse solution to obtain a definite change of blue litmus to a pink. Actually, the concentration of this final solution before extracting or draining the work should be about ½% or less of the volume of the rinse. The residual alkalinity must be overcome to prevent

dye migration during drying and also to deter subsequent brown cellulosic degradation staining on sweet stains or even on cotton or linen in the fabric being washed.

For dyesetting action during washing of wool and silk, acetic acid solutions from 1% to 4% may be required. In this case, special detergents which are not affected by acids are needed to remove soil.

In dyeing of wool and silk, acetic acid is probably the most popular dyeing assist. The concentration of the solution or dye bath, in this case, will vary according to the dyestuff used and the depth of value or brilliance of the color desired, probably less than one percent.

DILUTION TABLES

Initial % Acetic Acid	Parts Acetic Acid	Water	Approximate % final Solution
100 (glacial)	28 parts	72 parts	28%
56% Acetic Acid	1 part	1 part	28%
28% Acetic Acid	5 oz.	1 gal.	1%
28% Acetic Acid	10 oz.	1 gal.	2%
28% Acetic Acid	15 oz.	1 gal.	3%
28% Acetic Acid	20 oz.	1 gal.	4%
Vinegar 5%	1 part	4 parts	1%
Vinegar 5%	2 parts	3 parts	2%
Vinegar 5%	3 parts	2 parts	3%
Vinegar 5%	4 parts	1 part	4%

BORIC ACID

Boric Acid, H_3BO_3, in textile conservation is a relatively uncommon acid because it is one of the weakest, having at one percent concentration a pH of about 5. It is popular when, combined with borax in proper proportions, it forms a stable buffering solution very nearly neutral.

Also, a solution of 7 oz. of Boric acid and 10 oz. of Borax in one gallon of water will produce a sugar browning stain retardant.[1]

A similar solution is also recommended as a flame retardant when impregnated into a fabric and dried.[2]

Boric acid may be purchased in crystalline form 100% from drug stores or chemists. To use it, dissolve crystals in water at about 5 to 10% concentration; less if for medical purposes.

CITRIC ACID

Citric Acid, $HOOC\text{-}CH_2\text{-}HCOH\text{-}CH_2\text{-}COOH$, is an effective reducing agent sometimes employed as a rust removing agent on fabrics. It is a relatively strong acid which, if allowed to remain on a cellulosic fabric without complete rinsing or neutralization, will eventually cause acid degradation on the fiber. It may be useful for converting red rust on iron ornaments or perhaps ink writings on fabrics to the black sesqui state in a restoration problem. In this case, the black patina will eventually return to the red ferric state unless it is protected by a lacquer. When used, thorough rinsing with immediate drying is imperative before lacquering. The pure form is crystalline and may be obtained from drug stores or chemist shops. Concentrations of about 5 to 10% are suggested for use.

HYDROCHLORIC ACID

Hydrochloric Acid, H Cl, or Muriatic Acid as purchased for commercial usage, finds its chief use in cleaning stone walls and in removal of furnace scale from iron as in pickling. While in low concentrations, less than five percent, it may be used in wool dyeing and in separating wool from fiber mixtures or about 10% in fabric analysis procedures. At this last concentration, especially if heated, it will quickly dissolve cotton and most common forms of nylon.

Technical grade muriatic acid as used as a flux for soldering or for cleaning stone walls may be purchased at hardware stores. Analytical grade hydrochloric acid may be obtained from chemical supply firms.

Hydrochloric acid will damage silk fibers. It will also dissolve metal ornaments, except pure gold, and will damage silver.

FORMIC ACID

Formic Acid, HCOOH, is a volatile acid, more chemically active than acetic acid. Its pH at 0.1% to 1.0% registers 2.5 to 2.2 respectively [3] and might damage cotton if it did not evaporate quickly. In textile conservation its chief uses are in dyeing and as a reagent in fiber analysis procedures. A ten percent solution, which is a common concentration, is used for confirming presence of nylon in a mixed fiber fabric, since nylon dissolves in it; whereas, wool, cotton and linen do not. However, cellulose acetate also dissolves in it, while rayon does not.

It is an ingredient in paint strippers or softeners which helps to swell and soften hardened paints and prepares them for removal.

As the active ingredient in ant and bee venom, it may produce painful burns on the skin, especially where abraded.

It may be purchased from chemical supply houses as a ten percent solution.

HYDROFLUORIC ACID

Hydrofluoric Acid, H_2F_2, is a third volatile acid that finds wide usage in textile conservation. Its chemical activity is stronger than that of Formic acid, having a pH range of about 2.2 to 2.0 at 0.1 and 1.0 per cent concentration. This is low enough to damage cellulose and cause color changes in some dyes if the acid is not rinsed thoroughly soon after being used.

It is one of the few substances that will dissolve glass and for that reason it is used extensively for etching purposes. In this case, the areas of glass which are to remain clear are protected by waxes or other organic films during the etching processes. Because of this effect, hydrofluoric acid solutions are stored and dispensed in plastic bottles or utensils. Because it attacks most inorganic substances including metals, one should avoid using enamel, glass, stone ware or metal basins or utensils for containers or for spotting table tops.

Although it does not damage most fibers if used with care, it is a fairly strong reducing agent and may affect some dyes and colors. It will evaporate reasonably soon, but for safe results one should rinse it out thoroughly after use. Two reasons why are: first, if allowed to remain on cotton that has been weakened by ageing, it may produce irreversible fiber damage, especially in areas where the cotton or linen have developed old brown spots or stains; second, unless diluted and removed, the hydrofluoric acid will evaporate into the air and these fumes will etch glass or metal objects in a confined space or room. However, this acid is probably the most efficient and fastest rust and metallic oxide stain remover in our approved list of chemicals and, if used carefully, promises amazing results.

The fumes are toxic and breathing them in concentrated form is dangerous. If the acid solution comes in contact with skin, one should rinse it away at once.

Hydrofluoric acid is obtainable in plastic bottles with dropper nozzle in eight ounce sizes or less. There are a number of popular brands, such as "Erusticator", "Rust-mover", "Rust-ease", and many competing names. The concentration of these varies from 5% to 10% and of course the prices will vary accordingly. They are sold by laundry and cleaning supply firms in most large cities.

OXALIC ACID

Oxalic Acid, $H_2C_2O_4$ or HOOCCOOH, an organic acid found in a number of plants such as rhubarb and spinach, is marketed in a crystalline form which is actually $H_2C_2O_4 \cdot 2H_2O$. It is sparingly soluble in cold water but much more so in hot water. It is a reducing agent and will convert iron from the insoluble red ferric iron ionic state to the soluble, pale green, ferrous iron ionic state, which is essential in removing rust from fabrics. In many cases, where it might be inadvisable to use hydrofluoric acid because of presence of iron or glass ornaments or substances which would be immediately attacked by the hydrofluoric acid, oxalic acid may be useful. For best results, the solution must be hot and concentrated. A good example is in the case of cleaning rust stains from polished marble. Other acids will not only attack iron but also calcium, whereas calcium oxylate is insoluble and the marble is not appreciably affected while the iron is changed. In this case, it may be presumed that the oxalic acid may also act as a chelating agent in removal of the iron from the scene.

At any rate, oxalic acid is a popular ingredient in garment spotting compounds known as "General Formula" and is obtainable on the market from suppliers of cleaning and spotting chemicals. "General Formula" will be discussed later under spotting chemicals.

Unless rinsed thoroughly, oxalic acid may have two damaging effects on textiles. First, it is one of the strongest of the so-called weak acids and at reasonable concentrations, as might happen in drying, of 1% or greater produce a pH of 2 or stronger. At this acidity value cotton or linen are apt to deteriorate. Second, as the water evaporates and cools, the oxalic acid forms sharp needle-like crystals which have been accused of mechanically damaging the fibers of whatever class they may be.

If swallowed, this acid is a poison. In medicine it has been used for corn and callus removal. It should be rinsed immediately if it comes in contact with the skin.

It is obtainable from drug stores or chemists shops.

ACID SALTS

The acid salts may be considered along with the true acids because through the mechanism of hydrolysis they produce hydrogen ions (H^+) in solution. The ways in which hydrolysis works have been explained previously in our Principles of Textile Conservation Science No. VI, The Wonders of Water in Wetcleaning, *Textile Museum Journal*, Vol. II, No. 1, December 1966.

In the acid salts case the hydrogen ion concentration is limited by the generally low solubility of these compounds and the relatively few hydrogen ions that they produce when in solution. This in turn provides a built in safety control to supply hydrogen ions to a chemical action at a slow rate. This is a sort of buffering process and may be depended upon for maintaining a reasonably constant pH level, probably more so than the "weak" acid theory mentioned in describing the true acids.

LAUNDRY SOURS

Modern washing practices use a considerable amount of acid salts annually. In this industry, some of the more popular compounds form a class known as the "Fluoride Sours". These are the bifluorides of potasium KF·HF, sodium NaF·HF and ammonium NH_4F·HF. Their function in the process is to neutralize residual alkalinity from the sudsing cycle in washing cottons and to complete the removal of adsorbed hypochlorite bleach which, unless destroyed, will continue to oxidize the cotton beyond a reasonable result.

At a moderate acidity, the decomposition of the hypochlorite bleach is spontaneous and the oxidation threat ceases. Furthermore, unless the residual alkalinity from sudsing is neutralized, brown discolorations will begin to develop as the cotton or

linen ages. These points will be discussed later when alkalies and bleaches are described.

Where water for washing comes from deep wells, or from corroded piping, ferrous iron salts often occur as dissolved impurities. Souring with bifluorides is suggested in this case for preventing black and red iron deposits on the work when it is exposed to the air. This point will be explained in detail later under rust removers and cleaning of iron.

Salts of fluosilicic acid H_2SiF_6 form another group of popular laundry sours. These salts are generally known as silicofluorides although some writers prefer the term fluosilicates.

The "silicofluorides" which include ammonium silicofluoride $(NH_4)_2\ SiF_6$, sodium silicofluoride $Na_2\ SiF_6$, potassium silicofluoride K_2SiF_6 and zinc silicofluoride $ZnSiF_6$ may be procured from many laundry and cleaning chemical supply firms.

This particular group of acid salts is also used extensively for formulating water soluble insecticides. Of the four named above, zinc silicofluoride is the most popular, probably because it is relatively more soluble than the other members. It is widely used for moth proofing carpets and woolen goods. In these cases, it is dissolved at the rate of one and a half percent of the crystalline form in water and applied by spraying the goods lightly. If not dissolved out as in washing or wetcleaning, the treatment is long lasting and has not been accused of environmental poisoning to date.

Alum, an interesting double salt of potassium, aluminum and sulfuric acid with a chemical formula of K Al $(SO_4)_2 \cdot 12\ H_2O$ is strongly acid in solution. It finds considerable use in textile conservation as a dye setting agent, as a mordant in dyeing and in some cases in precipitating certain insoluble metallic soaps from soluble soap solutions when developing water proofing in fabrics. It is also used as a tawing agent or tanning substance for making white leathers. Because it can be washed out in wetcleaning, white leather gloves are best cleaned in dry solvents only. If for any reason, wetcleaning of white leathers must be attempted, the alum must be replaced.

When used as a mordant, the alum is deposited on the fiber and then steamed to convert it into basic aluminum hydroxide gel. The acid dye is then expected to form an insoluble lake color. The same mechanism is used in forming the insoluble metal soaps when water proofing a fabric. When replacing the tawing in white leather, steaming is forbidden because it causes excessive shrinkage and hardening of the leather.

There are many other acid salts but in most cases they are seldom used in cleaning or preservation of textiles and related substances.

NOTES

[1] *National Institute of Drycleaning Technical Bulletin T-335,* November 1954.

[2] Norbert J. Berg, *Wetcleaning,* page 220. National Association of Dyers and Cleaners, Silver Spring, Maryland, 1944.

[3] George P. Fulton, *Applied Science for Drycleaners,* page 56, Table IV, National Institute of Drycleaning, Silver Spring, Maryland, 1951.

PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. XIV

THE ALKALIES AND ALKALINE SALTS

JAMES W. RICE

In textile cleaning and conservation science, alkalies are defined as substances that produce hydroxyl ions (sometimes abbreviated to ^-OH) in water solution. Note that this electronic charge of the radical ^-OH is minus or negative. When the ^-OH meets with a positive H^+ which we know as a positive ion there is an immediate junction and a compound HOH or water is formed with the cancellation of the electrical charges. This is neutralization. In cleaning language, the alkalies are called sweeteners because they are used to control acids or sours.

However, alkalies are very important in cleaning work in other ways than just neutralization. They are used to adjust the pH value of cleaning solutions to the optimum level for good soil removal. For most cleaning problems, depending on the soil, the best pH working range is generally found between pH9 to pH 10.5. Below pH 9 soil removal is meagre with ordinary soaps and detergents. Above pH 10.5 soil removal may be very good but we would expect dye bleeding from colored goods and excessive shrinkage or even fiber damage in woolen fabrics. For white or unbleached cottons that are heavily soiled, pH levels of 11.4 may be required, but such cases are unusual in historic or fragile textile work.

Alkalies have the property of attacking certain fats, oils and greases to convert them into soluble soaps. This is called saponification and is a well known cleaning effect. Alkalies also aid in emulsifying mineral oils and greases which do not react